ZINC OXIDE AS A CONTACT MATERIAL FOR p-GaN

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ABSTRACT

The fabrication procedure of transparent and conducting ZnO films yielding ohmic contacts to p-GaN has been developed. The microstructure and electronic properties of p-GaN/ZnO interface were studied using atomic force and electron transmission microscopies, and x-ray photoelectron spectrometry. The observed ohmic behaviour is explained in terms of formation of a tunnelling p-GaN/ n^+-ZnO junction.

1. INTRODUCTION

Reliable, transparent ohmic p-type contacts are essential for the development of GaN-based LEDs and laser diodes. Hitherto, bilayer Ni/Au [1] or Pt-based metallizations [2, 3] of a thickness reduced to 5-10 nm have been used, albeit at the expense of increased contact resistivity and reduced long-term stability.
The transparent conducting oxides (TCOs), with their unique electro-optical properties, are the most likely candidates to overcome those thin-metal contacts shortcomings. Promising results with sputter deposited indium tin oxide (ITO) contacts to GaN have been achieved. Although these contacts exhibited non-linear behaviour [4], ITO-contacted LEDs showed uniform luminescence, indicating effective current-spreading and hole injection [5].
In this communication, we report on ZnO electrodes as high-transmittance and low resistivity ohmic contacts to p-GaN. We have chosen ZnO for its similarity to GaN in terms of crystalline structure, band gap energy and thermal stability. ZnO electrodes were fabricated by oxidation of vacuum deposited thin Zn films. The main goal of this study was to understand the relation between the consecutive processing steps and the final optical, electrical and structural characteristics of ZnO/p-GaN contacts.

2. EXPERIMENTAL

GaN (0001) samples used in this study were grown by metalorganic chemical vapour deposition method on sapphire substrate. 2 μm thick, p-type layers were Mg doped to the hole concentration of $1x10^{17}$ cm^{-3} and $5x10^{17}$ cm^{-3}.
The process steps used for the fabrication of ZnO contact were as follows. The samples were 5 min. cleaned in hot organic solvents followed by 20 min. etch in thiourea-based solution 10 % $(NH_2)_2CS$: HCl : 15% H_2O_2 = 20 :1 : 1 and immediately loaded into Leybold L 560 Universal Coating Unit. The unit was equipped with a sputtering station and resistance heated evaporators, and operated at a base pressure of $1x10^{-7}$Torr. The surface cleaning was completed by *in-situ* Ar^+ ion sputter etching at 300 V for 30 s. To anticipate poor adhesion of Zn to non-metallic substrates, an Au nucleation film was predeposited on the sample surface. Zn films of a thickness 50 to 100 nm were used throughout the experiments. Both Au and Zn were thermally evaporated. Zn oxidation was carried out by furnace annealing in O_2 flow, at 320^0C for 30 - 40 min. Finally, Au film for wiring purposes was deposited. Patterns for electrical measurements were fabricated by lift-off photolithography. Specific contact resistance was determined by circular transmission line method (cTLM).

The conductivity of thin ZnO films was assessed by measurements of sheet resistance and thermopower. Optical transmission of the films was determined by measuring the change of the intensity of monochromatically dispersed light of quartz-tungsten-halogen lamp detected by Si photodiode biased in reversed polarisation. For these measurements ZnO was deposited on double-side polished sapphire substrates.
The surface morphology was monitored by AFM using Digital Instruments Nanoscope IIIa in a tapping mode with Si tip. GaN/ZnO samples were prepared in cross-section for analysis by TEM. TEM images were obtained with a Topcon 002B microscope operating at 200 keV. The surface and interface chemistry of GaN/ZnO system were studied by XPS with a Physical Electronics PHI 5700 ESCA spectrometer, using monochromatised Al Kα (1486.6 eV) and non-monochromatised Mg Kα (1256 eV) radiation, respectively. The vacuum during the measurements was about 10^{-10} Torr. The atomic composition was obtained from Mg radiation spectra as for Al radiation the N (1s) line overlaps with the Ga LMM Auger lines. XPS allowed monitoring the shift of the Fermi level at p-GaN surface at different stages of the formation of GaN/ZnO interface through the Ga (3d) core level photoelectron spectroscopy.

3. RESULTS AND DISCUSSION

Electrical and optical properties

Zinc deposited at a pressure $1x10^{-7}$ Torr yielded, after oxidation, high resistivity ZnO. The thickness of oxidised zinc films was factor 1.2 higher as compared to that of as-deposited Zn. Conducting ZnO was obtained only after the working pressure during Zn evaporation has been increased above 10^{-6} Torr by back-filling the deposition chamber with high-purity nitrogen gas. Zn films deposited at $1 – 5\ x10^{-5}$ Torr enabled to form n^+-ZnO of a bulk resistivity $\rho \leq 10^{-3}\ \Omega$cm.
To evaluate the properties of conducting oxide as an electrical contact to p-GaN, Au pads were deposited on ZnO surface. It has been verified that n^+-ZnO/Au contacts were ohmic with a resistivity $\leq 10^{-5}\ \Omega cm^2$.
The ohmic behaviour of p-GaN/ZnO contacts was observed after the resistivity of ZnO films has been decreased to $\rho = 10^{-2}\ \Omega$cm. This corresponded to the specific contact resistance of $r_c = 1 \times 10^{-2}\ \Omega cm^2$ and $r_c = 5 \times 10^{-3}\ \Omega cm^2$ for contacts formed on p-GaN with free carrier concentration of $1x10^{17}\ cm^{-3}$ and $5x10^{17}\ cm^{-3}$, respectively. Further decrease of ZnO resistivity to $\rho \leq 10^{-3}\ \Omega$cm made it possible to fabricate contacts characterised by $r_c < 5 \times 10^{-3}\ \Omega cm^2$.
Optical transmission of ZnO films on sapphire was measured in the wavelength range 400-700 nm. The transmission of 60 nm thick ZnO exceeded 70% in the whole visible wavelength range, with a maximum of 78% at 500 nm. For 120 nm thick ZnO films the transmission was a few percent lower.

Morphology and structure

AFM and TEM studies provide insight into the development of the surface morphology during the fabrication of ZnO film on GaN substrate and the final structure of GaN/ZnO contact. Fig. 1 shows AFM images. At the initial GaN surface, after *ex-situ* wet cleaning and *in-situ* sputter-etching, a clear terrace structure characteristic of epitaxial GaN is visible. Au nucleation film forms an island-like structure. The rms roughness of such surface was ≈ 0.6 nm. After Zn deposition, the rms roughness was ≈ 7 nm, and further increased to ≈11 nm as a result of oxidation.
Cross-sectional TEM view of GaN/ZnO contact is presented in Fig. 2. The contact interface is smooth and abrupt with no signs of interaction between GaN and the metallization. The interface from the metallization side is composed of two phases. Using high resolution imaging, the small dark islands embedded in a light-coloured film were identified as crystalline Au dots set in hexagonal zinc oxide film.

Electronic properties

Fig. 3 shows the photoemission spectra of the Ga (3d) and Zn (3d) core levels from the initial p-GaN surface and after consecutive processing steps leading to the formation of p-GaN/ZnO ohmic contact. It should be noticed that the shift of Ga (3d) core levels resulting from Au and Zn deposition as well as Zn oxidation followed the same direction. The deposition of Au nucleation film induced a 0.7 eV shift of the Fermi level closer to the conduction band minimum, subsequent Zn deposition increased it by 0.1 eV, and oxidation of Zn caused further 0.4 eV Fermi level shift. It is commonly adopted [6, 7], that the shift of the binding energy of Ga (3d) core level represents the shift of the Fermi level, corresponding thus to the band bending at the interface. Consequently, the observed shift of

Fermi level induced by the formation of ZnO on p-GaN corresponds to downward band bending and amounts to 1.2 eV. The shift of the binding energy of Zn (3d) core level after oxidation of Zn corresponds to the formation of ZnO.

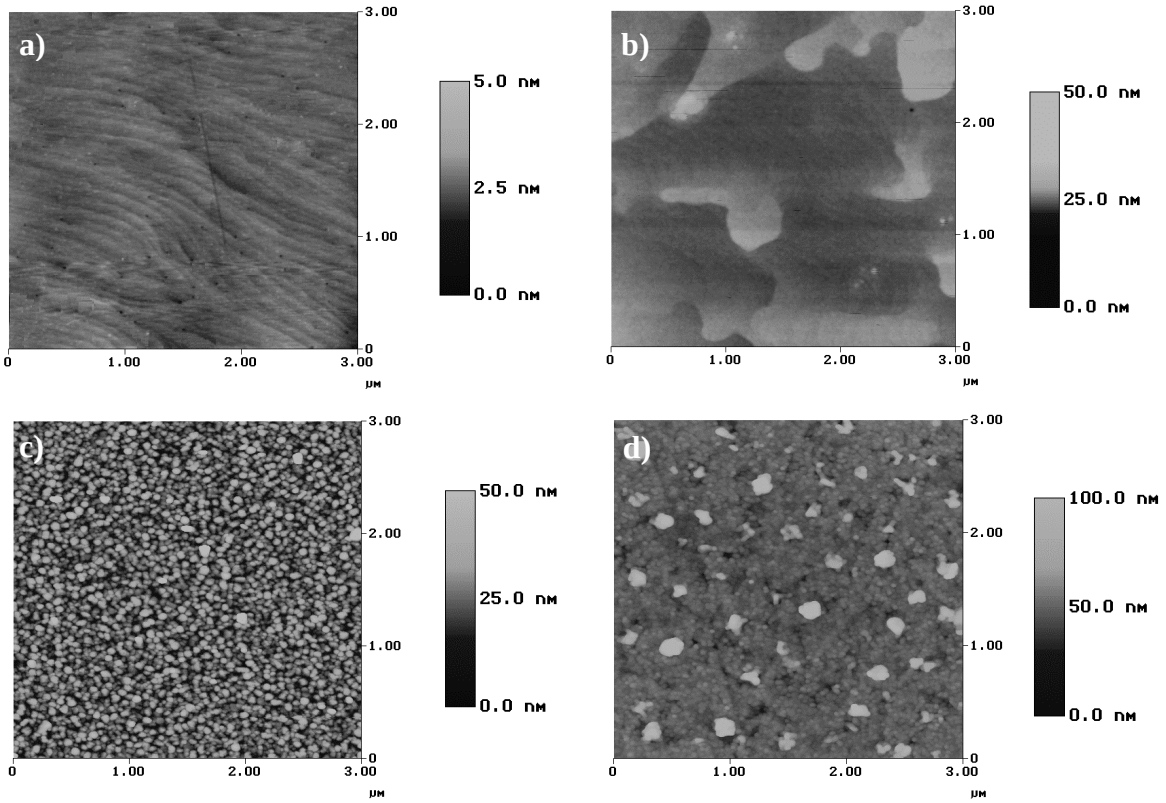

Fig. 1. AFM images showing the sample surface after consecutive steps of ZnO fabrication: (a) the initial GaN surface, (b) GaN surface with Au nucleation film, (c) the surface of as-deposited Zn film, (d) the surface of oxidised Zn film

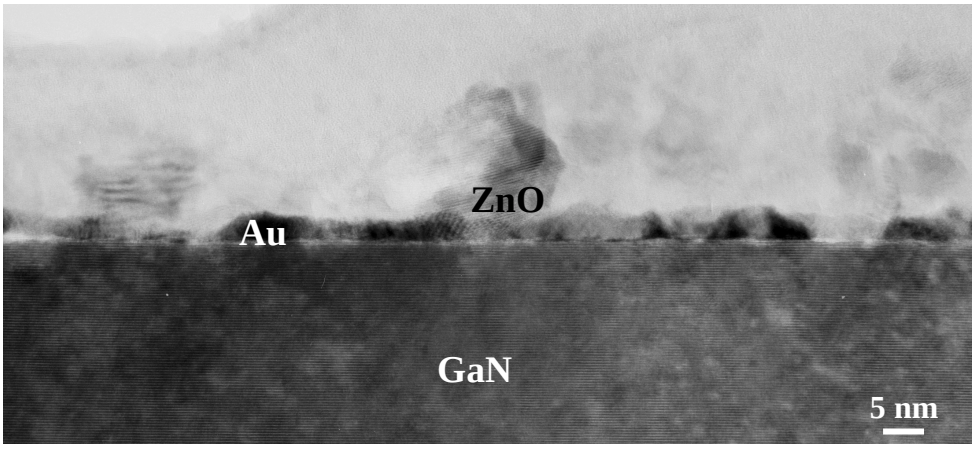

Fig. 2. Cross-sectional TEM micrograph of GaN/ZnO interface

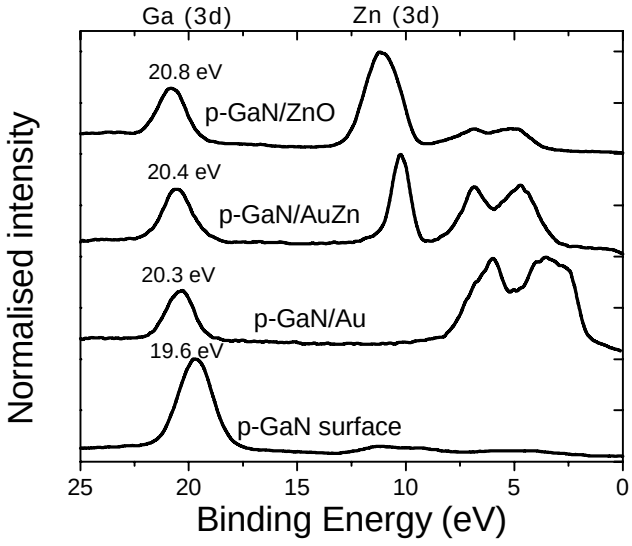

Fig. 3. Evolution of the Ga (3d) core level resulting from Au and Zn deposition, and Zn oxidation

4. CONCLUSIONS

We have developed a fabrication method of zinc oxide films suitable for obtaining transparent ohmic contacts to p-type GaN. The electro-optical properties of ZnO contacts compare favourably with those of metal-based [1] and ITO contacts [5]. Moreover, ZnO contacts are ohmic and transparent without additional thermal processing.

The novelty of our technological procedure, namely sequential steps of Au and Zn deposition followed by Zn oxidation was proven to play a crucial role for the final properties of p-GaN/ZnO contacts. The XPS analysis revealed that a strong downward band bending at p-GaN surface accompanied the formation of p-GaN/ZnO interface, with no evidence of interfacial reaction or intermixing. As for the interfacial region from ZnO side, it has been recently reported that thin films of TCOs such as In_2O_3, in spite of highly doped bulk, develop at the surface a substantial depletion layer [8]. This implies that, enhanced upward band bending at the n^+-ZnO side together with downward band bending at p-GaN side could give the explanation of the observed ohmic behaviour in terms of formation of a tunnelling p-GaN/ n^+-ZnO junction.

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